

ASARCO

CHM HILL

MEMORANDUM


1264392 - R8 SDMSWITH ATTACHMENTS
SEE DATA BASE

TO: Doug Lovell/DEN

FROM: Tom Sale/DEN

DATE: May 7, 1985

RE: ASARCO First Quarterly Groundwater Sampling Data,
January 15 through 21, 1985; Impact of Turbidity
on Metal Ion Concentrations

PROJECT: W68230.00

INTRODUCTION

Groundwater monitoring wells DH-1 through DH-11 at the ASARCO facility in East Helena, Montana, were sampled between January 15 through 21, 1985. Samples obtained from the wells contained large amounts of turbidity. Subsequent to the sampling, concerns regarding the turbidity and its effects upon the representativeness of total dissolved metal samples have been voiced by Systems Technology, Inc., Hydro-metrics, and the Montana State Department of Health and Environmental Sciences. These concerns center around the following issues:

1. Due to high turbidity, some metals samples were allowed to stand for 1 to 3 hours prior to preservation. During this time, exposure of the sample to an oxidizing environment and changes in sample pH may have significantly altered the chemical equilibrium of the samples and caused significant changes in concentrations of some dissolved metal ions.
2. Potentially the material imparting the turbidity to the samples has the ability to absorb metal cations from the aquifer water while desorbing cations which are less preferentially held. These surface reactions may have altered the dissolved metal ion concentrations of the samples.

The following discussion attempts to provide sufficient information to evaluate these issues. This includes: discussion of the physical processes involved with each issue, a review of pertinent literature, and conclusions

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regarding the representativeness of the January 1985 ground-water quality data. The final portion of this memorandum summarizes the information presented and provides recommendations concerning future samplings.

SAMPLE PRESERVATION

The effort of collecting a representative water quality sample is futile if chemical reactions occur that alter the character of the water between the time the sample is collected and analyzed. Commonly, the chemical environment of groundwater is reducing (lacking oxygen) and saturated with CO_2 . As a sample is removed from this environment to the surface, oxygen enters the sample, causing an increase in the oxidizing potential of the sample (Eh) and CO_2 will tend to gas out of the sample causing an increase in pH ($-\log[\text{H}^+]$).

Figure 1, copied from HEM (1970), presents a pH-Eh species predominance diagram for iron. The highlighted box in the center of the diagram shows the normal range of pH and Eh. The figure indicates that as pH and Eh increase insoluble ferric hydroxide ($\text{Fe}(\text{OH})_3$) becomes the dominant species. Most metal cations behave in a similar fashion with insoluble precipitates tending to form at high Ph and Eh values.

In order to inhibit the formation of insoluble metal precipitates during sample storage, the sample's pH is lowered to less than two. At this pH soluble metal cation species predominate (see Figure 1). If the parameter of interest is total dissolved metals, it is also necessary to filter water samples prior to acidification. If this is not done, large amounts of metal precipitates which exist in association with suspended solids will be dissolved and erroneous values of total dissolved metals will be obtained.

Water samples obtained from the ASARCO monitoring during the first samplings round contained high turbidity and required filtrations for determination of total dissolved metals. Some samples were allowed to settle from 1 to 3 hours to reduce the time and effort required for filtration. During this time the reaction previously discussed may have occurred and altered the metal ion concentrations in the samples.

Data presented in Hydrometric's letter of February 19, 1985, to John Nickel of ASARCO (Attachment A) shows the variations in sample pH with time for seven samples (Table 1). This

Figure 1

pH-Eh Species Predominance Diagram

for Iron

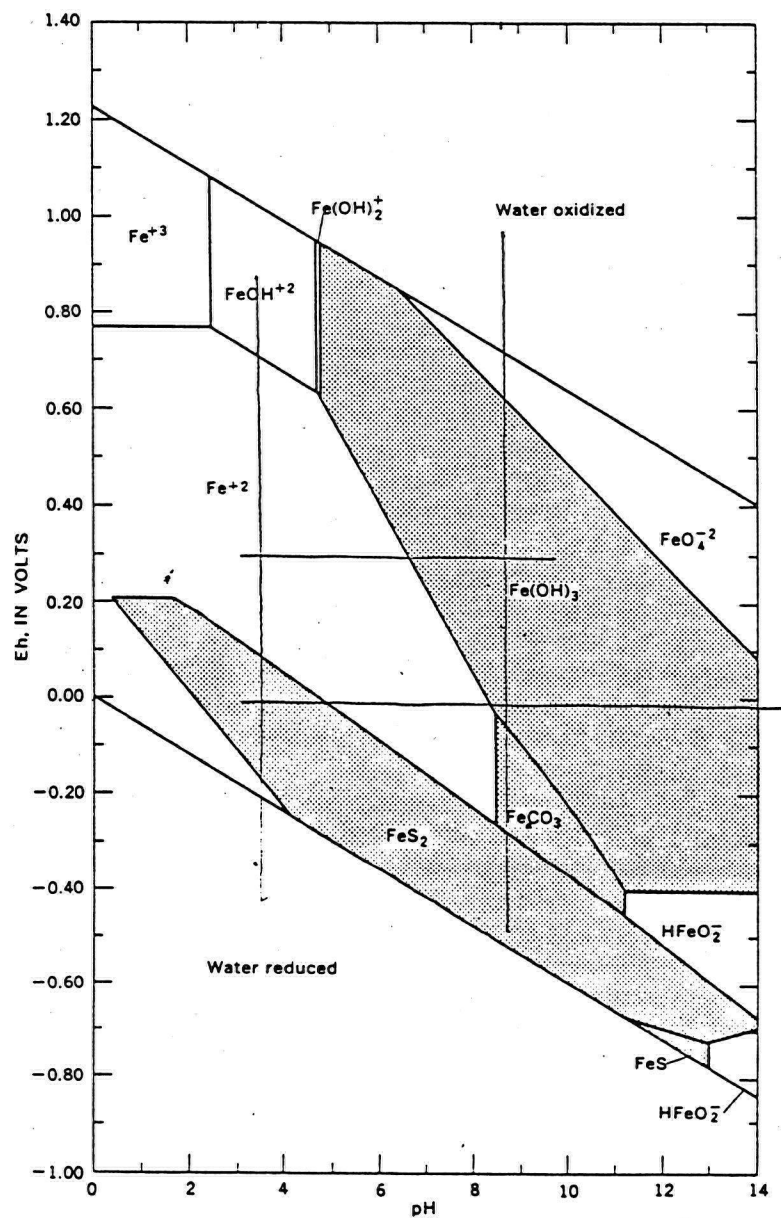


FIGURE 14.—Fields of stability for solid and dissolved forms of iron as function of Eh and pH at 25°C and 1 atmosphere of pressure. Activity of sulfur species 96 mg/l as SO_4^{2-} , carbon dioxide species 1,000 mg/l as HCO_3^- , and dissolved iron 0.0056 mg/l.

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data shows that out of seven samples, the pH of one decreased significantly after 45 minutes and two increased significantly after one day. One question raised by this data is whether the samples pH varied in the first 10 minutes. Personal experience has shown that pH values in some groundwater samples will increase rapidly in the first few minutes after sampling and then stabilize. Due to the lack of information on sample pH immediately after sampling, and the fact that some of the sample's pH varied with time, it is difficult to conclude what impact the delay in preservation had, with respect to chemical precipitation reactions controlled by pH.

Table 1
 PH MEASUREMENTS OVER TIME

Sample No.	Time Coll.	Date	pH	Δ pH	pH	Δ pH
			1st Read. (~10 min.)		3rd Read. (1 day)	
AEH-8501-118	9:30 a.m.	1/18/85	7.65	0	7.90	+ .25
AEH-8501-124	11:30 a.m.	1/18/85	7.70	+ .01	7.70	0.0
AEH-8501-117	12:30 p.m.	1/18/85	7.78	+ .01	7.88	+ .10
AEH-8501-122	3:00 p.m.	1/18/85	7.69	- .04	7.65	- .04
AEH-8501-125	4:30 p.m.	1/18/85	7.97	- .26	7.70	- .27
AEH-8501-121	9:30 a.m.	1/19/85	7.70	- .01	7.69	- .01
AEH-8501-126	4:20 p.m.	1/21/85	7.49	+ .03	7.55	+ .06

Note: In all cases, sample temperatures and buffer temperatures are the same.

Delays in sample preservation may also have allowed changes in sample Eh to cause precipitation reactions. This change in Eh would only be possible if a difference existed between the oxidation-reduction condition within the aquifer and the surface. Water quality data presented in the Systems Technology Inc. memorandum of April 30, 1985 (Attachment B), and copied in Table 2 suggest that the oxidation-reduction within the aquifer is similar to that of a surface water. This is indicated by the values of total iron (EPA) and dissolved iron (ASR). Large amounts of total iron are present in the sample, but only small amounts of dissolved iron (6.3 to 130 ug/e) exist in solution. These concentrations are typical of a surface water with a neutral pH. Since it

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appears that the sample Eh remained stable, it is likely that precipitation reactions associated with changes in Eh did not occur.

Table 2
COMPARISON OF USEPA & ASARCO METALS DATA

Well No.	As		Cd		Cu		Fe		Pb		Mn		Zn	
	EPA	ASR	EPA	ASR	EPA	ASR	EPA	ASR	EPA	ASR	EPA	ASR	EPA	ASR
DH-2	26	8.	<4.	<1.	61	28.	18,300	25.	45	<5.	247	19.	349	110
DH-3	7.8	7.	<4.	<1.	6.4	<8.	111	6.3	4.6	<5.	101	120	156	180
DH-3R	5.4	7.	<4.	3.	18.	<8.	5,780	25.	11	<5.	196	100	155	170
DH-7	99	5.	<4.	<1.	343	<8.	62,500	25.	51	<5.	4,390	41	341	11
DH-9	22,000	6.	500	5.	5,500	13.	219,000	130	26,000	<5.	12,400	2,800	48,100	580
DH-10	5,800	5,100	<24.	3.	156	9.	16,600	63	170	<5.	4,310	4,800	551	71

Work done by the Illinois State Water Survey, 1981, investigated the effects of delayed sample preservation upon the concentrations of seven metal cations. The results are presented in Table 3. These show that Ca, K, Mg, Mn, and Na were not significantly affected by the delays in sample preservation. This is not surprising due to the fact that these species tend to form insoluble precipitates only at high pH's and concentrations. In contrast, concentrations of Fe and Zn showed dramatic decreases with delays in sample preservation. Additional metal ions which may behave similar to Fe and Zn include Al, Cr, and Cu.

Based upon available information, it is not possible to quantitatively evaluate the impact of the delays in sample preservation which occurred during the first quarterly sampling round of groundwater monitoring wells at ASARCO. The only statement that can be made is that it is possible that significant changes in water chemistry occurred during the delays in sample preservation and that these changes in water chemistry may have allowed for precipitation reactions to occur which reduced the concentrations of some dissolved metal ions (i.e., Fe, Zn, Al, Cu, and Cr).

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Table 3
 SITE 5-BRD and 6-DUP: ANALYSIS OF THE TENTH WELL VOLUME
 SAMPLE USED FOR STORAGE STUDY
 (CONCENTRATIONS IN mg/L)

Site 5-BRD

Hours after collection- before preservation	pH	Ca	Fe	K	Mg	Mn	Na	Zn
0	6.7	111.	11.6	32	44.6	3.81	186	0.18
7	7.0	110.	0.33	31	41.9	3.15	172	0.02
24	7.0	104.	<0.03	35	41.4	3.10	181	0.02
48	7.0	99.	0.03	33	39.5	2.98	171	0.02

Site 6-DUP

Hours after collection- before preservation	pH	Ca	Fe	K	Mg	Mn	Na	Zn
0	6.8	32.5	5.74	189	94.2	ND*	215	ND*
7	7.2	35.2	<0.08	203	110.	ND*	242	ND*
24	7.2	32.0	<0.08	204	96.6	ND*	223	ND*
48	7.2	30.1	0.34	184	89.1	ND*	204	ND*

*ND = not detectable.

ADSORPTION-DESORPTION BY COLLOIDAL MATERIALS

Whenever a foreign object is introduced into an aqueous system it will tend to adsorb and/or desorb chemical constituents. This will continue until the rates of adsorption and desorption are equal and equilibrium is obtained. The amount of time required to reach equilibrium is a function the capacity of the foreign object to hold specific constituents, the concentrations of the constituents in the aqueous system, the amount of foreign material, and the volume of water which the object is exposed.

In the case of the groundwater monitoring wells constructed at ASARCO, objects such as PVC well screen, gravel pack, and potentially drill cuttings from above the zone of saturation were introduced into the groundwater system. PVC well screen

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and silica gravel pack have limited capacities to adsorb and store chemical constituent and should reach equilibrium with the surrounding water quickly.

Drill cuttings introduced from above the zone of saturation can absorb significant amounts of chemical constituents if they have high Cation Exchange Capacities (CEC) and exist in large quantities. If these conditions are met, drill cuttings will adsorb and desorb metal ions until sufficient aquifer water is flushed past the material for equilibrium to be reached. This may occur through natural groundwater flow, through bailing prior to samplings, and well development.

Due to the high turbidity observed in the ASARCO monitoring well samples, it has been suggested that the colloidal material associated with the turbidity is acting as a sink for metal cations. More specifically, that the cation exchange sites on the colloidal materials is preferentially adsorbing the small, more highly charged ions such as Cr^{+3} and Pb^{+2} in exchange for larger, less highly charged ions such as Na^{+} , Ca^{+2} , and Mg^{+2} .

This exchange of cations will only occur if the materials producing the turbidity is introduced from an area outside of the aquifer being monitored. All materials within the aquifer should be in equilibrium with the aquifer due to their long contact time with the aquifer water and its dissolved metals.

The monitoring wells at ASARCO were constructed using hollow stem and air rotary drilling methods. Neither of these drilling methods involved circulation of drill cuttings. Drill cuttings were removed directly from the hole either through the mechanical action of the auger or the air lift of the air rotary rig. This leads to the conclusion that the colloidal material observed in the well came from the saturated zone.

The worst case would be if all turbidity is caused by materials carried down from above the water table and that the material has a high cation exchange capacity. Under these conditions it is likely that this material would come to equilibrium quickly due to water carried through the material during well purging, well development, and by natural flow of groundwater during the one month between well completion and sampling.

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Attempts to estimate the volume of water required to bring a fixed amount of colloidal materials to equilibrium with the water quality were made. These calculations could not be made due to the complex chemical reaction involved. Despite this, it may be stated that adsorption and desorption of metal ions by colloidal material probably had little effect upon the water quality of the samples obtained from the groundwater monitoring wells. This statement can be made since it is likely only small amounts of material was introduced from above the water table and this material in all likelihood reached equilibrium with the formation water prior to sampling.

CONCLUSIONS AND RECOMMENDATIONS

The collection of representative samples from groundwater monitoring wells is not a straightforward or easily accomplished task. It requires careful consideration of the hydrologic and chemical conditions existing at each monitoring location. The questions concerning the representativeness of the groundwater samples obtained from ASARCO during the first quarterly sampling is a good case in point.

Due to delays which occurred between sample collection and preservation, the potential for metal ion precipitation and subsequent removal through filtration exists. The degree to which this occurred is difficult to assess due to a lack of data defining the samples' chemical characteristics (pH & Eh) immediately after sampling. At present it can only be stated that the samples have a potentially negative bias for some metal ions (metals concentrations less than actual).

More specific conclusions could be made if additional information is obtained on the amount of time each sample was allowed to stand prior to preservation, and under what conditions each sample was stored during this time.

Due to the high turbidity found in the monitoring wells, the potential for colloidal material to act as a sink for metal ions exists. Based upon the available information concerning the methods of drilling and the time between well completion and sampling, it appears that this is not an important issue. Still it is not possible to totally disregard this issue.

Additional information which would aid in evaluation of this issue includes the volumes of water removed during well

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development at each well and relative degrees of turbidity encountered at each well.

Since the representativeness of the water samples cannot be clearly established at this time, decisions must be made regarding resolution of the issues. Steps taken toward resolution of the issues should include:

- o Obtain the information mentioned in the previous paragraphs and attempt to identify specific wells where the issues discussed are important.
- o Compare the first quarter's analysis with future data to see if the results appear to be representative of the groundwater quality at each site.
- o If the data cannot be validated through these two steps, obtain another quarterly sample from the wells in January of 1986.

An additional option for resolution of the issues has been proposed by Hydrometrics in their letter to Mr. Gene Taylor of the EPA, April 12, 1985 (Attachment C). In this letter they propose to split metal samples. One split will be filtered and acidified, the other acidified and then filtered .5 to 1 hour later. Hydrometrics feels that this will "provide some information on the relationship between metal concentrations and turbidity." If no difference is seen between the samples it may be stated that neither the turbidity or the delays in sample preservation affected metal ion concentrations.

Hydrometrics' proposal has several limitations. First of all it seems unlikely that a significant difference will not exist between the samples. Secondly, the geochemical environment during the next sampling round may be very different from that which existed in January. Despite these limitations the idea does have merit and is worth considering.

In order to remove these issues from future groundwater samplings, the following recommendation is made:

All metals samples should be filtered and preserved immediately after sampling. If turbidity continues to inhibit sample filtration, two options are available. Step filtration system may be used. These systems use

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multiple filters of varying size and work quite effectively on turbid samples. If this is not feasible, a nondisruptive method of borehole evacuation should be used (i.e., bladder pump). Use of a bailer to evacuate a monitoring well will surge the well and disrupt sediments within the formation. Bladder pumps remove water at low rates (1 to 2 gallons per minute) and tend not to disrupt the sediments and, hence, yield samples with low turbidity.

REFERENCES

- Gibb, G. P., Schuller, R. M., and Griffin, R. A. 1981. Procedures for the Collection of Representative Water Quality Data From Monitoring Wells. Illinois State Water Survey, Cooperative Ground Water Report 7, Urbana, Illinois.
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- Scalf, M. R. (et al.). 1981. Manual of Ground-Water Sampling Procedures. U.S. Environmental Protection Agency, Ada, Oklahoma.

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